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Strain profiling of $HfO_2/Si(001)$ interface with high-resolution Rutherford backscattering spectroscopy

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Strain depth profiles in HfO_2 (3 nm)/Si(001) prepared by atomic-layer chemical vapor deposition have been measured using high-resolution Rutherford backscattering spectroscopy in combination with a channeling technique. It is found that the Si lattice is compressed in the vertical direction around the interface. The observed maximum strain is about 1% at the interface and the strained region extends down to ~3 nm from the interface.
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Physical dimensions of metal–oxide–semiconductor field effect transistors (MOSFETs) have been shrinking very rapidly. One of the key components of MOSFETs is SiO_2 used as gate oxide films. The interface between SiO_2 and Si(001) is known to be very abrupt and smooth, although there is a thin transition layer (a strained SiO_2 layer) in the SiO_2 side.[1–3] The successful downsizing of MOSFETs is in part attributed to the ideal properties of the $SiO_2/Si(001)$ interface. According to the International Technology Roadmap for Semiconductors, however, the thickness of gate oxide films for sub-100 nm MOSFETs should be less than 1.5 nm. This cannot be achieved with either SiO_2 or oxynitride films because of high tunneling currents through such thin films. To increase the capacitance while reducing the tunneling current, various kinds of high-*k* materials have been investigated as possible alternatives to SiO_2.[4] Among those materials, HfO_2 is one of the most promising candidates because of its high stability against thermal treatments.[5] In contrast to $SiO_2/Si(001)$, however, the interface structure of $HfO_2/Si(001)$ has not been characterized extensively. In the present letter, we report strain depth profiling of the $HfO_2/Si(001)$ interface using high-resolution Rutherford backscattering spectroscopy (HRBS).

A ultrathin HfO_2 film thickness of ~3 nm thick was prepared on *p*-type Si(001) by means of atomic-layer chemical vapor deposition (ALCVD) at 300 °C. The surface of Si(001) was precleaned by HF vapor *in situ* before the deposition. As a metal precursor and oxygen source, $HfCl_4$ and H_2O were used, respectively. The $HfO_2/Si(001)$ interface was observed *ex situ* with HRBS. The details of the HRBS are described elsewhere.[6] Briefly, a beam of 400 keV He^+ ions was collimated to 2×2 mm^2 and to a divergence angle less than 1 mrad. The collimated beam was incident on the $HfO_2/Si(001)$ sample which was mounted on a high-precision five-axis goniometer installed in an UHV chamber. Energy spectra of He^+ ions scattered at 50° were measured by a high-resolution magnetic spectrometer (the energy resolution is $\sim 1\times 10^{-3}$ and the acceptance angle is ~0.3 msr).

Figure 1 shows an example of the observed HRBS spectrum. There are hafnium and oxygen peaks at ~390 and at ~325 keV, respectively. A small peak seen at ~360 keV is attributed to Cl contamination in the interface region, which may originate from the $HfCl_4$ precursor. A calculated spectrum for HfO_2 (3 nm)/Si(001) is shown by a solid line. Although the width of the calculated Hf peak agrees with the observed one, the calculated oxygen peak is much narrower than the observed one. Moreover, the observed leading edge of Si is shifted toward lower energy than the calculated edge. These facts suggest that there is a SiO_x layer at the $HfO_2/Si(001)$ interface.

Elemental depth profiles for Hf, Si, O, and Cl were derived from the observed HRBS spectrum. The obtained results are shown in Fig. 2. A solid line shows twice the Hf concentration, which roughly agrees with the observed oxy-

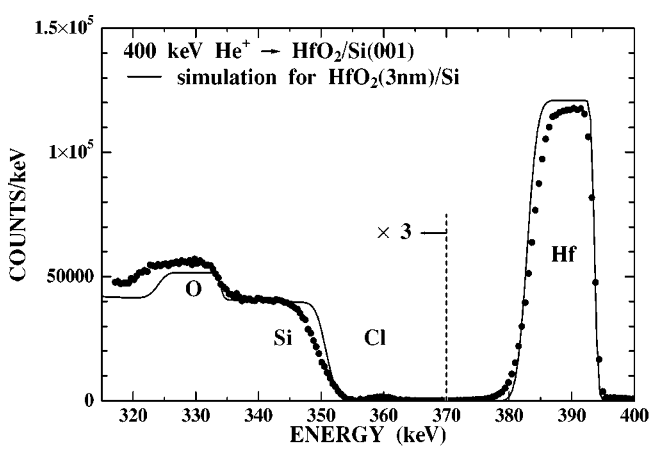

FIG. 1. High-resolution RBS spectrum of $HfO_2/Si(001)$ observed at a scattering angle of 50°. The incident ion is 400 keV He^+ and the incident angle is 50.24°. The solid curve shows a simulated spectrum for HfO_2 (3 nm)/Si(001).

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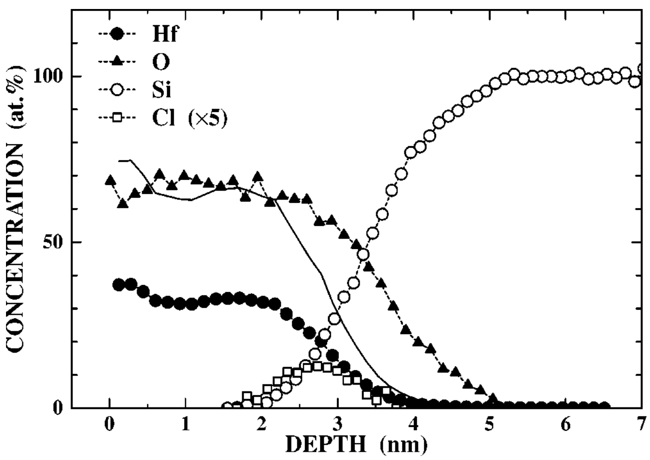

FIG. 2. Elemental depth profiles for Hf, Si, O, and Cl (×5) in HfO_2/Si(001). The solid curve shows twice the Hf concentration. There are excess oxygen atoms in the interface region, showing formation of a thin SiO_x layer between the almost stoichiometric HfO_2 film and Si substrate.

gen concentration. This indicates that an almost stoichiometric HfO_2 film was deposited by ALCVD. There are, however, excess oxygen atoms in the interface region, showing formation of a thin SiO_x layer between the HfO_2 film and Si(001).

An angular scan of HRBS spectrum around the [111] axis in the $(1\bar{1}0)$ plane was performed to measure the Si lattice strain. The observed HRBS spectrum was divided into a number of strips corresponding to different narrow depth regions of width 0.5 nm. Figure 3 shows the scattering yield for each Si strip as a function of incident angle relative to the [111] direction. The depth shown in Fig. 3 is measured from the HfO_2/SiO_x interface. A [111] channeling dip can be clearly seen except for very shallow depth regions which

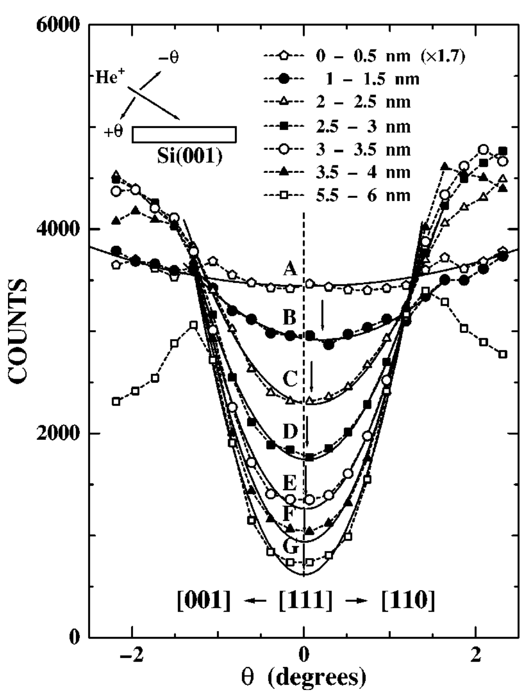

FIG. 3. Angular scan around [111] axis in $(1\bar{1}0)$ plane. The Si yields for different depth regions of 0.5 nm wide are shown as a function of the angle of incidence around the [111] channeling direction. The depth shown is measured from the HfO_2/SiO_x interface. The channeling dip shifts towards larger incident angle with decreasing depth.

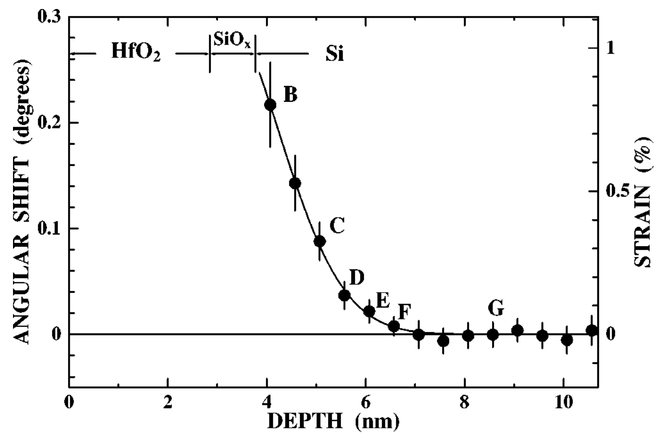

FIG. 4. Angular shift of the channeling dip as a function of depth from the surface. The axis on the right shows the local compressive strain estimated from the observed angular shift with Eq. (1).

corresponds to the SiO_x layer (e.g., curve A). Although the position of the channeling dip agrees with the bulk [111] axis at deeper regions (e.g., curves F and G) the dip position shifts toward larger incident angles with approaching to the interface. This indicates that Si lattice is compressed in the vertical direction around the interface region.

Figure 4 shows the observed angular shift of the channeling dip as a function of depth from the surface. The axis on the right shows the local compressive strain estimated by

$$\epsilon = \frac{2\Delta\theta_i}{\sin 2\theta_i}, \tag{1}$$

where $\theta_i = 54.74°$ is the angle of incidence for [111] channeling. The obtained compressive strain is about 1% near the SiO_x/Si interface, which corresponds to a stress of ~1 GPa. The strain decreases rapidly with increasing depth and becomes smaller than the detection limit (0.1%) of the present measurement at a depth about 3 nm from the SiO_x/Si interface. Because the thickness of the inversion layer in MOSFETs is comparable to the thickness of the observed strained layer, the stain may affect the performance of MOSFETs.

There are experimental evidences of a strained Si layer in the SiO_2/Si interfaces.[7–10] Measurements of optical second-harmonic generation spectra of oxidized Si suggested existence of a thin strained layer with expansion of Si–Si bond lengths close to the interface.[8] Spectroscopic ellipsometry also revealed the existence of a strained Si layer at the SiO_2/Si interface.[9] Considering the formation of the thin SiO_x layer at the interface, the strained Si layer observed in the present measurement could be related to the previously observed strained Si layer at the SiO_2/Si.

In summary, the interface region of the HfO_2/Si(001) grown by ALCVD was carefully characterized by high-resolution RBS. A thin SiO_x layer was found to be formed between the HfO_2 film and the substrate Si(001). Strain profiling of the Si lattice was performed by high-resolution RBS/channeling. The channeling dip for Si signal near the SiO_x/Si(001) interface was shifted towards larger incident angles, indicating the existence of compressive strain in the vertical direction. The observed maximum strain was about 1% and the strain decreases rapidly with increasing depth. The starin becomes less than the detection limit (~0.1%) at

$\sim$3 nm from the SiO_x/Si(001) interface. The observed strain may have a large effect on the carrier mobility if the HfO_2 is used as gate dielectrics in future MOSFETs.

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